



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US99/03097 <b>(22) International Filing Date:</b> 12 February 1999 (12.02.99)  <b>(30) Priority Data:</b> 60/074,639      13 February 1998 (13.02.98)      US  <b>(71) Applicant:</b> SOLUTIA, INC. [US/US]; 10300 Olive Boulevard, St. Louis, MO 63141 (US).  <b>(72) Inventors:</b> GOETTLER, Lloyd, A.; 3032 Killarney Drive, Pace, FL 32571 (US). LYSEK, Bruce, A.; 3449 Stefani Road, Cantonment, FL 32533 (US). JOARDAR, Saikat, S.; 946 Kiefer Trails Drive, Ballwin, MO 63021 (US).  <b>(74) Agent:</b> KAMMERER, Patricia, A.; Arnold White & Durkee, P.O. Box 4433, Houston, TX 77210 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS TO PREPARE A POLYMER NANOCOMPOSITE COMPOSITION  <b>(57) Abstract</b>  A process to prepare a polymer nanocomposite composition comprising forming a flowable mixture of a polyamide and a silicate material; dissociating at least about 50 % but not all of said silicate material; and subjecting the polyamide in the dissociated mixture to solid state polymerization to form the nanocomposite.		

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## **PROCESS TO PREPARE A POLYMER NANOCOMPOSITE COMPOSITION**

### **FIELD OF THE INVENTION**

This invention relates to a process to prepare a nanocomposite material comprising a  
5 polymer matrix having dispersed therein a silicate. More particularly, this invention relates to a  
process to prepare a nanocomposite material comprising forming a flowable mixture of a  
polyamide and a silicate material, dissociating the silicate, and subjecting the dissociated  
flowable mixture to a solid state polymerization step to produce the nanocomposite material.

### **CROSS-REFERENCE TO RELATED APPLICATIONS**

10 The present application claims the benefit of U.S. Provisional Application Serial No.  
60/074,639, filed February 13, 1998.

### **BACKGROUND OF THE INVENTION**

International Application WO 93/04118 discloses a process of preparing a polymer  
nanocomposite having platelet particles dispersed therein. The process involves melt-processing  
15 the polymer with a swellable and polymer-compatible intercalated layered material and  
subjecting it to a shear rate sufficient to dissociate the layers. The layered material is  
compatibilized with one or more "effective swelling/compatibilizing agents" having a silane  
function or an onium cation function.

International Application WO 93/04117 discloses a process of preparing a polymer  
20 nanocomposite having platelet particles dispersed therein, where the polymer and the swellable  
and polymer-compatible intercalated layered material are melt-processed; The layered material is  
compatibilized with one or more "effective swelling/compatibilizing agents" selected from  
primary ammonium, secondary ammonium and quaternary phosphonium ions. The selected  
swelling/compatibilizing agents "...render their surfaces more organophilic than those  
25 compatibilized by tertiary and quaternary ammonium ion complexes...", facilitate exfoliation,  
resulting in less shear in mixing and less decomposition of the polymer, and heat stabilize the  
composite more than other cations (such as quaternary ammonium cation)  
swelling/compatibilizing agents.

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International Patent Application WO 94/22430 discloses a nanocomposite composition having a polymer matrix comprising at least one gamma phase polyamide, and dispersed in the polyamide is a matrix of a nanometer-scale particulate material. The addition of the particulate material to nylon 6 resulted in an improvement of flexural modulus and flexural strength (from 7  
5 to 35%), when compared to unfilled nylon 6. The addition of the particulate material to nylon 6,6 resulted in very little improvement (1 to 3%) of flexural modulus and flexural strength when compared to unfilled nylon 6,6.

International Patent Application WO 93/10098 discloses a polymer composite made by melt-processing a polymer with swellable and polymer-compatible intercalated layered material  
10 comprising layers having reactive organo- silane species covalently bonded to their surfaces.

International Patent Application WO 95/14733 discloses a method of producing a polymer composite that does not demonstrate melting or glass transition by melt-processing a polymer with a layered gallery-containing crystalline silicate. The examples include intercalated sodium silicate and a crystalline poly(ethylene oxide), montmorillonite intercalated with a  
15 quaternary ammonium and polystyrene, and montmorillonite intercalated with a quaternary ammonium and nylon 6.

International Patent Application WO 98/29499 discloses polyester nanocomposite compositions containing clay particles. The clay particles are preferably synthetic or chemically modified.

20 U.S. Patent No. 4,889,885 (issued December 26, 1989) describes a composite of a non-polyamide resin and a dispersed layered silicate. The silicate is treated with an onium salt ion exchange, and added to a monomer or oligomer.

U.S. Patent No. 5,514,734 (issued May 7, 1996) describes polymer composites containing layered or fibrillar particles derivatized with organosilanes, organotitanates, or  
25 organozirconates. Composite materials are characterized by thickness, diameter, and interlayer distances.

International Patent Application WO 93/11190 describes a polymer composite containing an exfoliated material derivatized with a reactive organosilane. Polymers are added prior to mixing in an extruder.

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International Patent Application WO 94/11430 describes gamma crystalline phase polyamides containing dispersed layered inorganic materials.

EPO application 0 358 415 A1 describes a polyamide resin containing a dispersed layered silicate which has been treated with an organic cation of a lactam as a swelling agent.

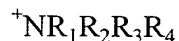
Japanese Kokai Patent No. SHO 62[1987]-252426 describes polymerization of a nylon 6 monomer in the presence of a silicate. The cooling rate of the polymer is controlled to achieve particular crystalline structures in the resulting composite.

None of the above references, alone or in combination, disclose the present invention, as claimed.

## SUMMARY OF THE INVENTION

This invention relates to a process to prepare a polymer nanocomposite composition suitable for automotive, electronic, film and fiber applications, where a combination of tensile strength, tensile modulus and flexural modulus are required. Additionally, the claimed polymer nanocomposite composition has a desirable surface appearance, toughness, ductility and dimensional stability. The composition processes well and tolerates a wide range of molding conditions.

The present invention relates to a process to prepare the above polymer nanocomposite composition comprising forming a flowable mixture of a polyamide and a silicate material and dissociating (as that term is described in more detail below) at least about 50% but not all of the silicate, and subjecting the polyamide in the dissociated flowable mixture to a solid state polymerization step. Optionally, the silicate is a silicate material treated with at least one ammonium ion of the formula:



wherein:

$R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  are independently selected from a group consisting of a saturated or unsaturated  $C_1$  to  $C_{22}$  hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where  $R_1$  and  $R_2$  form a N,N-cyclic ether. Examples include saturated or unsaturated alkyls, including alkylene; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxys, amino alkyls, acid alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls

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and substituted aryls, such as alkylaryls, alkyoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like. Optionally, one of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is hydrogen. The milligrams of treatment per 100 grams of silicate (MER) of the treated silicate, described in more detail below, is preferably from about 10 milliequivalents/100 g below the cation exchange capacity of the untreated silicate to  
5 about 30 milliequivalents/100 g above the cation exchange capacity of the untreated silicate.

An additional embodiment of the invention relates to nanocomposite compositions comprising a polyamide and a silicate. The polyamide may have a concentration of amine groups at least 10 mole % greater than the concentration of the carboxylic acid end groups. Preferably the polyamide has a weight average molecular weight in the range of about 30,000 D  
10 to about 40,000 D. Alternatively, the polyamide may have a weight average molecular weight of at least 40,000 D.

A further embodiment is directed towards a nanocomposite composition comprising a polyamide and a silicate, wherein the silicate is treated with an ammonium ion of the formula:  
 $^+NR_aR_bR_cR_d$ ; wherein  $R_a$ ,  $R_b$  and  $R_c$  is hydrogen (H) and  $R_d$  includes a carboxylic acid  
15 moiety.

The composite polymer matrix material of the present invention demonstrates, when tested, an improvement in tensile modulus and flexural modulus, without a substantial decrease in tensile strength or toughness when compared to that of the polymer without the silicate.

### DESCRIPTION OF THE FIGURES

20 The following figures form part of the present specification and are included to further demonstrate certain aspects of the present invention. The invention may be better understood by reference to one or more of these drawings in combination with the detailed description of specific embodiments presented herein.

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Figure	Description
1	Molecular weight effects with 7 w/o 2M2HT-montmorillonite
2	Molecular weight effect on nanocomposite stiffness 7 w/o 2M2HT-montmorillonite
3	Stress vs. strain graph, without SSP
4	Stress vs. strain graph, with SSP
5	Intrinsic viscosity vs. solid state polymerization time graph
6	Intrinsic viscosity vs. time at 220°C graph
7	UTS vs. % ash vs. SSP graph
8	eu vs. SSP vs. % ash graph
9	Notched Izod vs. Mw vs. SSP graph
10	Un-notched Izod vs. Amine/Acid vs. SSP graph
11	E vs. SSP vs. % ash graph

### DETAILED DESCRIPTION OF THE INVENTION

Polyamides of the present invention are synthetic linear polycarbonamides characterized by the presence of recurring carbonamide groups as an integral part of the polymer chain which are separated from one another by at least two carbon atoms. Polyamides of this type include polymers, generally known in the art as nylons, which can be obtained from diamines and dibasic acids having the recurring unit represented by the general formula:



in which  $R_5$  is an alkylene group of at least 2 carbon atoms, preferably from about 2 to about 11 or arylene having at least about 6 carbon atoms, preferably about 6 to about 17 carbon atoms;

and  $R_6$  is selected from  $R_5$  and aryl groups. Also, included are copolyamides, terpolyamides and the like obtained by known methods, for example, by condensation of hexamethylene diamine and a mixture of dibasic acids consisting of terephthalic acid and adipic acid. Polyamides of the above description are well-known in the art and include, for example, poly(hexamethylene adipamide) (nylon 6,6), poly(hexamethylene sebacamide) (nylon 6,10), poly(hexamethylene isophthalamide), poly(hexamethylene terephthalamide), poly(heptamethylene pimelamide) (nylon 7,7), poly(octamethylene suberamide) (nylon 8,8), poly(nonamethylene azelamide) (nylon 9,9), poly(decamethylene sebacamide) (nylon 10,9), poly(decamethylene sebacamide) (nylon 10,10), poly[bis(4-amino cyclohexyl)methane-1,10-decanecarboxamide], poly(m-xylene adipamide), poly(p-xylene sebacamide), poly(2,2,2-trimethyl hexamethylene terephthalamide), poly(piperazine sebacamide), poly(p-phenylene terephthalamide), poly(metaphenylene

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isophthalamide), and copolymers and terpolymers of the above polymers. Additional polyamides include nylon 4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons and their copolymers.

Other useful polyamides are those formed by polymerization of amino acids and derivatives thereof, as for example, lactams. Illustrative of these useful polyamides are poly(caprolactam) (nylon 6), poly(4-aminobutyric acid) (nylon 4), poly(7-aminoheptanoic acid) (nylon 7), poly(8-aminooctanoic acid) (nylon 8), poly(9-aminononanoic acid) (nylon 9), poly(10-aminodecanoic acid) (nylon 10), poly(11-aminoundecanoic acid) (nylon 11), poly(12-aminododecanoic acid) (nylon 12) and the like.

The preferred polyamide is Vydyne<sup>®</sup> nylon, which is poly(hexamethylene adipamide) (nylon 6,6), which gives a composite with the desired combination of tensile strength, tensile modulus and flexural modulus for the applications contemplated herein (Vydyne<sup>®</sup> is a registered trademark of Solutia Inc.).

The preferred molecular weight of the polyamide is in the range of about 30,000 to about 80,000 D (weight average) with a more preferred molecular weight in the range of about 30,000 to about 40,000 D. The most preferred molecular weight of the polyamide is at least about 40,000 D (weight average). Increasing the weight average molecular weight of the polyamide from about 35,000 to about 55,000 D results in an unexpected increase in toughness as indicated by the notched Izod impact test. Whereas an increase in the weight average molecular weight of from about 35,000 to about 55,000 D in the polyamide neat results in a small increase in toughness, the same increase in molecular weight in the nanocomposite results about twice the increase in toughness. Therefore, the increase in toughness is enhanced in the nanocomposite when compared to that of the polyamide neat.

In a preferred embodiment, the polyamide has an amine end group/acid end group ratio greater than one (1). More preferably, the concentration of amine end groups is at least 10 mole % greater than the concentration of the carboxylic acid end groups. In an even more preferred embodiment, the polyamide has a concentration of amine end groups at least 20 mole % greater than the concentration of the carboxylic acid end groups, and in a most preferred embodiment, the polyamide has a concentration of amine end groups at least 30 mole % greater than the



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concentration of the carboxylic acid end groups. In another embodiment, the concentration of amine end groups is essentially equal to the concentration of carboxylic acid end groups.

Among the preferred embodiments is nylon 6, nylon 6,6, blends thereof and copolymers thereof. The range of ratios of the nylon 6/nylon 6,6 in the blends is from about 1/100 to 100/1.

5 Preferably, the range is from about 1/10 to 10/1. The range of ratios of the nylon 6/nylon 6,6 in the copolymers is about 1/100 to 100/1. Preferably, the range is from about 1/10 to 10/1.

Optionally, the nanocomposite composition comprises at least one additional polymer. Examples of suitable polymers include polyethyleneoxide, polycarbonate, polyethylene, polypropylene, poly(styrene-acrylonitrile), poly(acrylonitrile-butadiene-styrene), poly(ethylene  
10 terephthalate), poly(butylene terephthalate), poly(trimethylene terephthalate), poly(ethylene naphthalate), poly(ethylene terephthalate-co-cyclohexane dimethanol terephthalate), polysulphone, poly(phenylene oxide) or poly(phenylene ether), poly(hydroxybenzoic acid-co-ethylene terephthalate), poly(hydroxybenzoic acid-co-hydroxynaphthenic acid), poly(esteramide), poly(etherimide), poly(phenylene sulfide), poly(phenylene terephthalamide).

15 The mixture may include various optional components which are additives commonly employed with polymers. Such optional components include surfactants, nucleating agents, coupling agents, fillers, impact modifiers, chain extenders, plasticizers, compatibilizers, colorants, mold release lubricants, antistatic agents, pigments, fire retardants, and the like.

Suitable examples of fillers include carbon fiber, glass fiber, kaolin clay, wollastonite,  
20 mica and talc. Suitable examples of compatibilizers include acid-modified hydrocarbon polymer, such as maleic anhydride-grafted propylene, maleic anhydride-grafted polypropylene, maleic anhydride-grafted ethylenebutylene-styrene block copolymer. Suitable examples of mold release lubricant includes alkyl amine, stearamide, and di-or tri- aluminum stearate.

25 Suitable examples of impact modifiers include ethylene-propylene rubber, ethylene-propylene diene rubber, methacrylate-butadiene-styrene (with core-shell morphology), poly(butylacrylate) with or without carboxyl modification, poly(ethylene acrylate), poly(ethylene methacrylate), poly(ethylene acrylic acid), poly(ethylene acrylate) ionomers, poly(ethylene methacrylate acrylic acid) terpolymer, poly(styrene-butadiene)block copolymers,

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poly(styrene-butadiene-styrene)block terpolymers, poly(styrene-ethylene/butylene-styrene) block terpolymers and poly(styrene-ethylene/butylene-styrene carboxylate) block terpolymers.

Suitable coupling agents include silane, titanate and zirconate coupling agents. Silane coupling agents are well-known in the art and are useful in the present invention. Examples of  
5 suitable coupling agents include octadecyltrimethoxysilane, gamma-aminopropyltriethoxysilane, gamma-aminopropyltrimethoxysilane, gamma-aminopropylphenyldimethoxysilane, gamma-glycidoxypropyl tripropoxysilane, 3,3-epoxycyclohexylethyl trimethoxysilane, gamma-propionamido trithoxysilane, N-trimethoxysilylpropyl-N(beta-aminoethyl) amine, trimethoxysilylundecylamine, trimethoxysilyl-2-chloromethylphenylethane,  
10 trimethoxysilylethylphenylsulfonlazide, N-trimethoxysilylpropyl-N,N,N-trimethylammonium chloride, N-(trimethoxysilylpropyl)-N-methyl-N,N-diallylammonium chloride, trimethoxysilylpropylcinnamate, 3-mercaptopropyl trimethoxysilane, 3-isocyanatopropyltriethoxysilane, and the like. The preferred silane is gamma-aminopropyltriethoxysilane. The silane coupling agent is optionally added to the polymer  
15 composite in the range of about 0.5 to about 5 weight % of the layered silicate. The preferred concentration range of silane coupling agent is about 1 to about 3 weight % of the layered silicate in the composite.

In one embodiment, the nanocomposite composition further comprises a composition wherein an end group of the polyamide is bonded to a surface of the treated silicate by a silane  
20 coupling agent.

The silicate materials of the present invention are selected from the group consisting of layered silicates and fibrous, chain-like silicates, and include phyllosilicates. Examples of fibrous, chain-like silicates include chain-like minerals, for example sepiolite and attapulgite, with sepiolite being preferred. Such silicates are described, for example, in Japanese Patent  
25 Application Kokoku 6-84435 published October 26, 1994.

Examples of layered silicates include layered smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, Laponite<sup>®</sup> synthetic hectorite, natural hectorite, saponite, sauconite, magadiite, and kenyaite; vermiculite; and the like. Other useful materials include layered illite minerals such as ledikite and admixtures of illites with one or

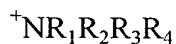
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more of the clay minerals named above. The preferred layered silicates are the smectite clay minerals such as montmorillonite, nontronite, beidellite, volkonskoite, Laponite<sup>®</sup> synthetic hectorite, natural hectorite, saponite, sauconite, magadite, and kenyaite.

The layered silicate materials suitable for use in the present invention are well-known in the art, and are sometimes referred to as "swellable layered material". A further description of the claimed layered silicates and the platelets formed when melt processed with the polyamide is found in International Patent Application WO 93/04117, which is hereby incorporated by reference. The layered silicate materials typically have planar layers arrayed in a coherent, coplanar structure, where the bonding within the layers is stronger than the bonding between the layers such that the materials exhibit increased interlayer spacing when treated.

The layered silicate materials may be treated as described in more detail below with the subject ammonium ion to enhance the interlayer swelling and/or spacing useful for the performance of the treated silicate of the present invention. As used herein the "inter layer spacing" refers to the distance between the faces of the layers as they are assembled in the treated material before any delamination (or exfoliation) takes place. The preferred clay materials generally include interlayer or exchangeable cations such as Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and the like. In this state, these materials have interlayer spacings usually equal to or less than about 4 Å and only delaminate to a low extent in host polymer melts regardless of mixing. In the claimed embodiments, the cationic treatment is a ammonium species which is capable of exchanging with the interlayer cations such as Li<sup>+</sup>, Na<sup>+</sup>, Ca<sup>2+</sup>, K<sup>+</sup>, Mg<sup>2+</sup> and the like in order to improve delamination of the layered silicate.

The treated silicate of the present invention is a silicate material as described above which is treated with at least one ammonium ion of the formula



wherein:

R<sub>1</sub>, R<sub>2</sub>, R<sub>3</sub> and R<sub>4</sub> are independently selected from a group consisting of a saturated or unsaturated C<sub>1</sub> to C<sub>22</sub> hydrocarbon, substituted hydrocarbon and branched hydrocarbon, or where R<sub>1</sub> and R<sub>2</sub> form a N,N-cyclic ether. Examples include saturated or unsaturated alkyls, including alkenes; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxys, amino alkyls, acid

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alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls and substituted aryls, such as alkylaryls, alkoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like. Optionally, one of  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  is hydrogen. A mixture of two or more ammonium ions is contemplated by the present invention.

5 In an embodiment of the present invention,  $R_1$  is selected from the group consisting of hydrogenated tallow, unsaturated tallow or a hydrocarbon having at least 6 carbons, and  $R_2$ ,  $R_3$  and  $R_4$  independently have from one to eighteen carbons. Tallow is composed predominantly of octadecyl chains with small amounts of lower homologues, with an average of from 1 to 2 degrees of unsaturation. The approximate composition is 70%  $C_{18}$ , 25%  $C_{16}$ , 4%  $C_{14}$  and 1%  
10  $C_{12}$ . In another preferred embodiment of the present invention,  $R_1$  and  $R_2$  are independently selected from the group consisting of hydrogenated tallow, unsaturated tallow or a hydrocarbon having at least 6 carbons and  $R_3$  and  $R_4$  independently have from one to twelve carbons.

Examples of suitable  $R_1$ ,  $R_2$ ,  $R_3$  and  $R_4$  groups are alkyl such as methyl, ethyl, octyl, nonyl, tert-butyl, ethylhexyl, neopentyl, isopropyl, sec-butyl, dodecyl and the like; alkenyl such  
15 as 1-propenyl, 1-butenyl, 1-pentenyl, 1-hexenyl, 1-heptenyl, 1-octenyl and the like; cycloalkyl such as cyclohexyl, cyclopentyl, cyclooctyl, cycloheptyl and the like; alkoxy such as ethoxy; hydroxyalkyl; alkoxyalkyl such as methoxymethyl, ethoxymethyl, butoxymethyl, propoxyethyl, pentoxybutyl and the like; aryloxyalkyl and aryloxyaryl such as phenoxyphenyl, phenoxyethyl, phenoxydecyl, phenoxyoctyl and the like; arylalkyl such as benzyl, phenylethyl, 8-phenyloctyl,  
20 10-phenyldecyl and the like, alkylaryl such as 3-decylphenyl, 4-octylphenyl, nonylphenyl and the like.

Suitable ammoniums used in treating the silicate materials include oniums such as dimethyldi(hydrogenated tallow) ammonium, dimethylbenzyl hydrogenated tallow ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium, trimethyl hydrogenated tallow  
25 ammonium, methylbenzyldi(hydrogenated tallow) ammonium, N,N-2-cyclobutoxydi(hydrogenated tallow) ammonium, trimethyl tallow ammonium, methyldihydroxyethyl tallow ammonium, octadecylmethyldihydroxyethyl ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium and mixtures thereof. Particularly preferred ammoniums include quaternary ammoniums, for example, dimethyldi(hydrogenated

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tallow) ammonium, dimethylbenzyl hydrogenated tallow ammonium, methyldihydroxyethyl tallow ammonium, octadecylmethyldihydroxyethyl ammonium, dimethyl(ethylhexyl) hydrogenated tallow ammonium and mixtures thereof.

The treatment with the ammonium ion(s), also called "cationic treatments", includes  
5 introduction of the ions into the silicate material by ion exchange. In the embodiment where the silicate material is a layered silicate, the cationic treatments may be introduced into the spaces between every layer, nearly every layer, or a large fraction of the layers of the layered material such that the resulting platelet layers comprise less than about 20 particles in thickness. The platelet layers are preferably less than about 8 particles in thickness, more preferably less than  
10 about 5 particles in thickness, and most preferably, about 1 or about 2 particles in thickness.

The treated silicate has a MER of from about 10 milliequivalents/100 g below the cation exchange capacity of the untreated silicate to about 30 milliequivalents/100 g above the cation exchange capacity of the untreated silicate. The MER is the milliequivalents of treatment per 100 g of silicate. Each untreated silicate has a cation exchange capacity, which is the  
15 milliequivalents of cations available for exchange per 100 g of silicate. For example, the cation exchange capacity of the layered silicate montmorillonite can be about 95, and the exchange capacity of sepiolite is in the range of about 10 to about 20. When the MER of the treated silicate substantially exceeds the cation exchange capacity, there is an excess of cationic treatment which may be available to react with the polyamide. This excess may cause  
20 degradation of the properties of the polyamide.

The higher the MER, the lower the concentration of silicate in the treated silicate. Therefore, a first nanocomposite sample may have a higher concentration of treated silicate but a lower concentration of silicate, than a second nanocomposite sample, because the first sample has a higher MER than the second sample.

25 If the MER value of the treated silicate is substantially less than its exchange capacity, for example about 85 MER for the preferred montmorillonite, there is too little of the cationic treatment to have a beneficial effect. If the MER exceeds about 125, the excess ammonium may be detrimental to the properties of the nylon. Preferably, when the untreated montmorillonite

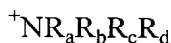
- 12 -

has an exchange capacity of about 95, the treated layered silicate has a cation exchange capacity of from about 85 to about 125.

The amount of silicate included in the composition is in the range of about 0.1 to about 12 weight % of the composite. The concentration is adjusted to provide a composite polymer matrix material which demonstrates, when tested, an increase in tensile modulus and flexural modulus, without a substantial decrease in tensile strength. Preferably, the increase in tensile modulus and flexural modulus is at least about 10%. More preferably, the increase in tensile modulus and flexural modulus is at least about 20%. Too little silicate fails to provide the desired increase in tensile modulus and flexural modulus. Too much silicate provides a polyamide composite with a decreased tensile strength. Further, it may be desirable to have the crystalline regions of the polyamide in the nanocomposite composition be less than about 1.0  $\mu\text{m}$ .

The particle size of the silicate is such that optimal contact between the polymer and the silicate is facilitated. The range of particle size can vary from about 10 microns to about 100 microns. Preferably, the particle size is in the range of from about 20 to about 80 microns. Most preferably, the particle size is below about 30 microns, such as those that pass through 450 mesh screens, in that the resulting polymer nanocomposite has improved performance properties.

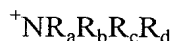
Optionally, the silicate can be treated with one or more ammonium ions of the formula



wherein at least one of  $\text{R}_a$ ,  $\text{R}_b$  and  $\text{R}_c$  is hydrogen (H) and  $\text{R}_d$  is selected from a group consisting of a saturated or unsaturated  $\text{C}_1$  to  $\text{C}_{22}$  hydrocarbon, substituted hydrocarbon and branched hydrocarbon. Examples include saturated or unsaturated alkyls, including alkylenes; substituted alkyls such as hydroxyalkyls, alkoxyalkyls, alkoxys, amino alkyls, acid alkyls, halogenated alkyls, sulfonated alkyls, nitrated alkyls and the like; branched alkyls; aryls and substituted aryls, such as alkylaryls, alkyoxyaryls, alkylhydroxyaryls, alkylalkoxyaryls and the like. As the definition of the  $\text{R}_d$  group for the ammonium ion above is generally the same as the definition for the  $\text{R}_4$  group in the ammonium ion, the Examples set forth above for the  $\text{R}_4$  group are also exemplary of the  $\text{R}_d$  group.

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In a separate embodiment,  $R_a$ ,  $R_b$  and  $R_c$  are hydrogen (H), and the  $R_d$  group contains a carboxylic acid moiety such that the ammonium ion



is an amino acid, for example 12-aminolauric acid ammonium. In this embodiment, it is

5 particularly preferred that the amine end groups/acid end groups ratio of the polyamide is greater than one (1) .

Optionally, the above ammonium ions may be mixed with at least one quaternary ammonium ion, said mixture used to treat the silicate. The quaternary ammonium ion preferably has a hydrocarbon chain. The hydrocarbon chain may be saturated or unsaturated. The  
10 hydrocarbon chain may be obtained from a natural source such as tallow, or from a synthetic source such as a synthesized or purified  $C_{12}$ ,  $C_{14}$ ,  $C_{16}$ , or  $C_{18}$  chain. A preferred mixture includes at least one of dimethyldi(hydrogenated tallow) ammonium, methyl dihydroxyethyl tallow ammonium, dimethylbenzyl hydrogenated tallow ammonium and/or dimethyl(ethylhexyl) hydrogenated tallow ammonium, either alone or in combination with 12-aminolauric acid  
15 ammonium.

Optionally, the silicate can be further treated with azine cationic dyes, such as nigrosines or anthracenes. Said cationic dyes would impart color-fastness and uniformity of color in addition to increasing the intercalation of the polymer molecules.

It is further desirable to have a polymer composite that provides both the desired strength  
20 and flexibility, and yet is lightweight. This is accomplished by minimizing the concentration of silicate in the nanocomposite. The preferred nanocomposite contains a concentration of silicate of from about 0.1 to about 12.0 weight % of the composite. The most preferred nanocomposite contains a concentration of silicate of from about 0.5 to about 6.0 weight % of the composite.

In a first embodiment of the present invention, the nanocomposite composition is  
25 prepared using a three step process. One step includes forming a flowable mixture of the polyamide as a polymer melt and the silicate material. The second step includes dissociating at least 50% but not all of the silicate material. The term "dissociating", as utilized herein, means delaminating or separating the silicate material into submicron-scale structures comprising individual or small multiple units. For the embodiment wherein layered silicates are utilized this

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dissociating step includes delaminating the silicate material into submicron scale platelets comprising individual or small multiple layers. For the embodiment wherein fibrous, chain-like silicates are utilized, this dissociating step includes separating the silicate material into sub-micron scale fibrous structures comprising individual or small multiple units.

5           As referred to in the mixture forming step, a flowable mixture is a mixture which is capable of dispersing dissociated silicate material at the submicron scale. A polymer melt is a melt processable polymer or mixture of polymers which has been heated to a temperature sufficiently high to produce a viscosity low enough for submicron scale mixing to occur. The process temperature should be at least as high as the melting point of the polyamide employed  
10 and below the degradation temperature of the polyamide and of the organic treatment of the silicate. The actual extruder temperature may be below the melting point of the polyamide employed, because heat is generated by the flow. The process temperature is high enough that the polymer will remain in the polymer melt during the conduct of the process. In the case of a crystalline polyamide, that temperature is above the polymer's melting temperature. For  
15 example, a typical nylon 6, having a melting point of about 225°C, can be melted in an extruder at any temperature equal to or greater than about 225°C, as for example between about 225°C and about 260°C. For nylon 6,6 a temperature of preferably from about 260°C to about 320°C is normally employed.

          Conventional methods can be employed to form the flowable mixture. For example, the  
20 flowable mixture can be prepared through use of conventional polymer and additive blending means, in which the polymer is heated to a temperature sufficient to form a polymer melt and combined with the desired amount of the silicate material in a granulated or powdered form in a suitable mixer, as for example an extruder, a Banbury<sup>®</sup> type mixer, a Brabender<sup>®</sup> type mixer, Farrell continuous mixers, and the like.

25           In one embodiment, the flowable mixture may be formed by mixing the polyamide with a previously formed silicate-containing concentrate. The concentrate includes the silicate and a polymer carrier. The concentration of the silicate material in the concentrate, and the amount of concentrate are selected to provide the desired silicate concentration for the final nanocomposite composition. Examples of suitable polymers for the carrier polymer of the concentrate include



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polyamide, ethylene propylene rubber, ethylene propylene diene rubber, ethylene-ethylacrylate, ethylene-ethylmethacrylate or ethylene methacrylate. Examples include Iotek<sup>®</sup> ionomer and Escor<sup>®</sup> ATX acid terpolymer, both available from Exxon. The polyamide polymers suitable for the carrier polymer include nylons such as nylon 6, nylon 6,6, nylon 4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons and their copolymers. The polymer of the carrier may be the same as or different from the polyamide of the flowable mixture. For example, both polymers may be a polyamide, particularly nylon 6,6, but may have the same or different molecular weight. The preferred weight average molecular weight of the carrier polymer of the concentrate is in the range of about 5,000 D to about 60,000 D. The most preferred range of the weight average molecular weight for the carrier polymer is in the range of about 10,000 to about 40,000 D. In this embodiment, the dissociation step of the present process, as described below, may occur at least in part via the forming of the concentrate such that the dissociation step may precede the step of forming the flowable mixture. It is therefore understood that the process steps (e.g., forming and dissociating) may occur sequentially without regard to order, simultaneously or a combination thereof. In the second step, the flowable mixture is sufficiently mixed to form the dispersed nanocomposite structure of dissociated silicate in the polymer melt, and it is thereafter cooled. The silicate can be dissociated by being subjected to a shear having an effective shear rate. As used herein, an effective shear rate is a shear rate which is effective to aid in dissociation of the silicate and provide a composition comprising a polyamide matrix having silicate substantially homogeneously dispersed therein without substantially breaking the individual units (e.g., platelets or fibrous chains).

Any method which can be used to apply a shear to a flowable mixture or any polymer melt can be used. The shearing action can be provided by any appropriate method, such as by mechanical means, by thermal shock, by pressure alteration, or by ultrasonics. Preferably, the flowable polymer mixture is sheared by mechanical methods in which portions of the melt are caused to flow past other portions of the mixture by use of mechanical means such as stirrers, Banbury<sup>®</sup> type mixers, Brabender<sup>®</sup> type mixers, Farrel<sup>®</sup> continuous mixers, and extruders. Most preferably, the mixture is subjected to multiple shearings. In addition to the increased shear provided by multiple shearing, increased residence time is also provided, which results in

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improved performance properties. Another procedure employs thermal shock in which shearing is achieved by alternatively raising or lowering the temperature of the mixture causing thermal expansions and resulting in internal stresses which cause the shear. In still other procedures, shear is achieved by sudden pressure changes in pressure alteration methods; by ultrasonic  
5 techniques in which cavitation or resonant vibrations which cause portions of the mixture to vibrate or to be excited at different phases and thus subjected to shear. These methods of shearing flowable polymer mixtures and polymer melts are merely representative of useful methods, and any method known in the art for shearing flowable polymer mixtures and polymer melts may be used.

10 Shearing can be achieved by introducing the polymer pellets at one end of the extruder (single or twin screw) and receiving the sheared polymer at the other end of the extruder. A preferred twin screw extruder is a co-rotating fully intermeshing type, such as the ZSK series manufactured by Werner and Pfleiderer Company. The silicate can be fed into the twin screw extruder at the feed throat or at the downstream vent. The preferred method is to feed the silicate  
15 at the downstream vent, which produces a composite polymer with improved performance properties.

Another preferred continuous compounder is the Farrel Continuous Mixer (FCM). For composites using Vydene<sup>®</sup> 21 nylon, the preferred temperature of the melt is in the range from about 275 to 315°C, with the most preferred range being from about 275 to 295°C.

20 The polymer melt containing nano-dispersed dissociated silicate material may also be formed by reactive extrusion in which the silicate material is initially dispersed as aggregates or at the nanoscale in a liquid or solid monomer and this monomer is subsequently polymerized in an extruder or the like. Alternatively, the polymer may be granulated and dry mixed with the treated silicate material, and thereafter, the composition may be heated in a mixer until the  
25 polymer is melted forming the flowable mixture.

The third process step is a solid state polymerization step, wherein the compounded pellets are held for several hours at a high temperature at least about 20°C below the melting or softening point of the polymer. For example, for nylon 6 and nylon 6,6, typical solid state polymerization conditions are heating the solid polymer in the range of about 200°C to about

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240°C for a period of from about 2 to about 5 hours. It is desirable to remove water produced during polymerization, e.g. by a dry nitrogen stream. Said additional process step results in an increase in molecular weight and an improvement in toughness, ductility and tensile strength of the nanocomposite.

5       The solid state polymerization step can be further effected with a catalyst that increases the molecular weight of the polyamide, e.g., a phosphorous-containing catalyst such as monosodium phosphate. Such phosphorous-containing catalysts are disclosed in U.S. Patent No. 4,966,949. For the composites that include a catalyst, milder treatment conditions are needed to effect the desired polymerization. For example, the treatment temperature can be below the  
10   temperature used in solid state polymerization absent the catalyst using the same polyamide, i.e., more than 20°C below the melting or softening point of the polyamide. The treatment time can be lowered to the range of about 0.5 hours to about 5 hours.

      An optional processing step is a heat treatment step, where the composition is heated to improve intercalation of the nylon molecules into the silicate structure. Said heat treatment step  
15   is performed by heating the composition at a temperature in the range of about 200°C to about 240°C for a period of about 2 to about 5 hours. The heat treatment step can optionally be incorporated into the dissociating step by increasing the residence time of the mixture in the mixer or extruder, thereby heat treating under melt conditions.

      The process to form the nanocomposite is preferably carried out in the absence of air, as  
20   for example in the presence of an inert gas, such as argon, neon or nitrogen. The process can be carried out in a batchwise or discontinuous fashion, as for example, carrying out the process in a sealed container. Alternatively, the process can be carried out in a continuous fashion in a single processing zone, as for example, by use of an extruder, from which air is largely excluded, or in a plurality of such reaction zones in series or in parallel.

25       In another embodiment of the present invention, the process to prepare a polymer nanocomposite composition comprises forming a first flowable mixture of a polyamide, at least one monomer and a silicate material; dissociating at least 50% but not all of the silicate material; polymerizing the monomer; and subjecting the polyamide in the mixture to solid state polymerization. It is to be understood that the polymerization of the monomer step can occur

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simultaneously or sequentially with one or more other steps in the process of this embodiment. Preferably, at least one monomer of the this embodiment includes monomers such as  $\epsilon$ -caprolactam, lauryllactam, and their corresponding lactones.

In yet another embodiment of the present invention, the process to prepare a polymer  
5 nanocomposite composition comprises forming a flowable mixture of a polyamide and a treated silicate material; dissociating the at least about 50% but not all of the treated silicate material; adding an additional amount of said polyamide, most preferably during said dissociating step; and subjecting the polyamide in the mixture to solid state polymerization.

Each of the above embodiments of the process to prepare the polymer nanocomposite  
10 composition can be followed by additional steps or treatments, or additional melt polymerization of the composition by increasing the residence time in the mixer with the removal of water condensation product. The increased residence time can also improve the intercalation of the polyamide into the silicate, as discussed above.

The composition of the present invention may be made into, but is not limited to, the  
15 form of a fiber, film or a molded article.

Solid state polymerization increases toughness, strength, and ductility of the produced polymer, while generally maintaining processability and modulus. Solid-state polymerization may improve properties such as elongation at yield, tensile elongation at break, flexural modulus, elastic modulus and both notched and unnotched Izod impact strength. Additional  
20 catalysts may be added, but are not required. Acid-functional clay treatments are particularly amenable to SSP (e.g., SCPX 1016 and SCPX 1255). They may serve to build polymer-clay linkages by tethering nylon molecules to the adsorbed acid moieties. The stoichiometric balance of amine and acid groups can impact the properties of the resulting polymer. A higher amine:acid ratio in the nylon is desirable, especially in the case of aminoacid-treated silicates.  
25 The use of solid state polymerization to finish the nanocomposite would allow starting with a lower RV nylon that would enhance intercalation, leading to greater exfoliation of the clay layers. The inherent brittleness of nanocomposites compounded on the FCM may be overcome with SSP finishing, to make the FCM a viable low cost process alternative.

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The following examples are included to demonstrate preferred embodiments of the invention. It should be appreciated by those of skill in the art that the techniques disclosed in the examples which follow represent techniques discovered by the inventors to function well in the practice of the invention, and thus can be considered to constitute preferred modes for its practice. However, those of skill in the art should, in light of the present disclosure, appreciate that many changes can be made in the specific embodiments which are disclosed and still obtain a like or similar result without departing from the spirit and scope of the invention.

### EXAMPLES

#### Materials:

The following types of nylon 6,6 polymers have been employed in nanocomposites described herein.

#### NYLON MATRIX RESINS

Designation	Weight-Average MW (kDaltons)	Amine End Group Conc. $\mu$ moles/g	Acid End Group Conc. $\mu$ moles/g
a	35	55	60
b	35	45	70
c	50	40	40
d	21	125	70

The montmorillonite clay used has an exchange capacity of about 95 milliequivalents per 100 g of silicate.

#### Example 1: Conventional compounding without SSP

A high molecular weight in the nylon matrix of nanocomposites has been found to be even more beneficial for the ductility and toughness of the nanocomposites than for the neat nylon polymer. The smectic silicates reduce nylon molecular weight during the compounding operation, especially in the first pass, resulting in a loss of ductility and toughness. For example, the molecular weight of nylon b was observed to drop from 36,500 to 31,500 D in a single pass of 7% montmorillonite treated with dimethyl di(hydrogenated tallow) ammonium cation (2M2HT-montmorillonite) through a 40 mm ZSK twin screw extruder manufactured by Krup Werner & Pfleiderer Company. A second pass reduced the MW further to only 21,000 D. The

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second pass under dry conditions could instead improve mechanical performance both due to molecular weight building as well as enhanced exfoliation and dispersion of the nano-platelets.

Solid state polymerization (SSP) can be implemented in compounded nanocomposites under similar conditions used for the neat polymer as a more efficient method for building molecular weight. Improvements are obtained in tensile strength and elongation, as well as notched and un-notched Izod impact strength. Slight losses in modulus sometimes occur, perhaps due to breakage of the thin delaminated platelets during flow of the higher viscosity nylon matrix.

#### Effects of molecular weight

The effects of the nylon 6,6 molecular weight or its equivalent relative solution viscosity (RV) on mechanical properties are shown in Figures 1 and 2 for nanocomposites prepared by conventional compounding in a twin screw extruder without subsequent SSP. The nylon RV is that of the raw material fed to the extruder. P1 and P2 in Figure 2 refer to the first and second passes through the compounder.

A higher amine/ carboxyl end group ratio on the nylon is preferable for nanocomposites, including those that are later subjected to SSP. The inherent Lewis acidity of the clay surface in combination with any acidity introduced from clay treatment, either in the form of an amino acid cation or the polyacrylate peptizer used on some clay grades, could alter the end group balance of the nylon, resulting in some degree of depolymerization. For example, an acidity of 40  $\mu\text{equiv/g}$  (4.0 mequiv/100g clay)  $-\text{COOH}$  was measured for both acrylate-coated Na-montmorillonite and the 2M2HT-montmorillonite. Amino acid exchanged grades would have higher acid levels according to the degree of substitution, as measured by the milliequivalent exchange ratio (MER) in milliequivalents of cation per 100 g of silicate. Thus, nylons a, and c are preferred to nylon b. The higher amine end group concentration of nylon d would be especially important in the case of silicates treated with amino acid cations, which can react with the amine end groups of the nylon. These treated silicates show a stronger response to the effects of SSP, resulting in larger increases in the above properties than nanocomposites containing pristine silicates or those treated with unreactive moieties.

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The molecular weight changes to the high amine nylon d due to compounding with 4% montmorillonite exchanged with 12-aminolauric acid (ALA-montmorillonite) and subsequent solid state polymerized have been analyzed via GPC.

Sample	Mw	Mn	Mw/Mn	IV	% Soluble
Nylon d flake	28.4	17.9	1.59	1.33	99.2
Nylon d extruded	30.3	19.7	1.54	1.38	100.
Nylon d + 4% ALA-montmorillonite	31.3	19.6	1.60	1.27	92.3
above + SSP 3 hr @ 220°C	84.2	37.2	2.26	2.75	70
Nylon d + SSP 3 hr @ 220°C	highly gelled - could not be run				

The symbols used in this table have the following meaning:

Mw: weight-average molecular weight

Mn: number-average molecular weight

IV: intrinsic viscosity measured in formic acid

#### Example 2: Solid state polymerization (SSP)

The extrusion process is seen in the above table to not change the molecular weight or its distribution in the nylon significantly. While a large increase in molecular weight of the nanocomposite does occur during SSP, it is reduced from that of the neat resin (which gels) by the presence of the acid moieties on the clay. There is, furthermore, evidence that the nylon matrix is being bound to the clay even during the compounding operation. During solid state polymerization, the nylon either branches or couples further with the organosilicate to form very high molecular weight species that become insoluble.

Solid state polymerization was practiced by heating the plastic pellets to 200-240°C (typically 220°C) with a dry nitrogen sweep to remove the water of condensation for a period of 2-4 hours (typically 4 hours). It was not necessary to add additional catalysts above those present from the initial melt polymerization, although mono- or di- sodium phosphate could have been added at 100-500 ppm. In one instance, adding 1,000 ppm monosodium phosphate resulted in an increase of compounded molecular weight from 27,400 to 30,600 D (SSP was not performed).

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Typically, the SSP dryer is set to 470°F (243°C) oil temperature and the nylon nanocomposite is heated for four hours at 220°C (230°C shell temperature) following an approximately 2-hour heat-up period. The resulting time-temperature profiles are shown below for representative nanocomposite solid state polymerization runs.

5

6.6% wt. 2M2HT-montmorillonite in nylon a solid-state polymerized for five hours

Time	Resin Temp. (°C)	Shell Temp. (°C)	Oil Temp., °F (°C)
7:15	0	0	520 (271)
8:15	140	150	480 (249)
9:15	210	225	480 (249)
10:00	223	227	480 (249)
11:00	220	226	470 (243)
12:00	220	226	470 (243)
13:00	220	226	470 (243)
14:00	220	226	470 (243)
15:00	220	226	470 (243)

3.7% wt. 2M2HT-montmorillonite in nylon a solid-state polymerized for four hours

Time	Resin Temp. (°C)	Shell Temp. (°C)	Oil Temp., °F (°C)
9:15	0	0	470 (243)
9:45	72	90	470 (243)
10:15	143	145	470 (243)
10:45	173	185	470 (243)
11:10	192	200	470 (243)
12:15	217	225	470 (243)
12:20	220	225	470 (243)
13:20	220	225	470 (243)
14:20	220	225	470 (243)
15:20	220	225	470 (243)
16:20	220	225	470 (243)

3.7% wt. 2M2HT-montmorillonite in nylon a solid-state polymerized for five hours

Time	Resin Temp. (°C)	Shell Temp. (°C)	Oil Temp., °F (°C)
7:30	0	0	600 (316)
8:30	140	160	600 (316)
10:15	223	227	470 (243)
11:15	220	226	470 (243)
12:15	220	226	470 (243)
13:15	220	226	470 (243)
14:15	220	226	470 (243)
15:15	220	226	470 (243)



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4.0% wt. ALA-montmorillonite in nylon a solid-state polymerized for three hours

Time	Resin Temp. (°C)	Shell Temp. (°C)	Oil Temp., °F (°C)
7:40	0	0	500 (271)
8:40	140	150	500 (271)
9:40	205	224	500 (271)
10:40	220	227	480 (249)
11:40	220	226	470 (243)
12:40	220	226	470 (243)
13:40	220	226	470 (243)

12.2% wt. montmorillonite treated with dimethyl benzyl hydrogenated tallow ammonium cation (2MBHT-montmorillonite) in nylon c, solid-state polymerized for four hours

Time	Resin Temp. (°C)	Shell Temp. (°C)	Oil Temp., °F (°C)
8:30	0	0	500 (271)
9:30	140	160	500 (271)
10:30	215	225	470 (243)
11:00	220	226	470 (243)
12:00	220	226	470 (243)
13:00	220	226	470 (243)
14:00	220	226	470 (243)
15:00	220	226	470 (243)

8.4% wt. 2MBHT-montmorillonite in nylon c solid-state polymerized for two hours

Time	Resin Temp. (°C)	Shell Temp. (°C)	Oil Temp., °F (°C)
7:30	0	0	500 (271)
8:30	200	215	480 (249)
9:30	215	226	470 (243)
10:00	220	226	470 (243)
11:00	220	226	470 (243)
12:00	220	226	470 (243)

5

6.2% wt. 2M2HT-montmorillonite in nylon b solid-state polymerized for three hours  
650 ppm of monosodium phosphate, monobasic, as catalyst

Time	Resin Temp. (°C)	Shell Temp. (°C)	Oil Temp., °F (°C)
8:15	0	0	500 (271)
9:15	145	150	500 (271)
9:45	185	185	400 (204)
10:15	185	190	400 (204)
11:15	185	190	400 (204)
12:15	190	190	400 (204)
13:15	190	190	400 (204)

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Example 3: Introduction of ductility

An example of the introduction of ductility through SSP is shown by the stress-strain curves (Figures 3 and 4) for 4.0 w/o ALA-montmorillonite in nylon a.

Example 4: Increase in molecular weight

5 Increasing molecular weight of the nylon matrix is indicated by the intrinsic viscosity measurements shown in the table below.

Intrinsic viscosity vs. SSP Time

Sample	0 hours	3 hours
4% sepiolite in nylon d		2.04

Intrinsic viscosity builds linearly with time in the SSP dryer, as for example shown by the following data and graph (Figure 5).

Resin	Organo clay	Organoclay (% wt.)	S.S.P. Time (hours)	Intrinsic Viscosity dl/g	Carboxyl	Amine	Mn	Mw
Nylon a	2M2HT-montmorillonite	3.7	0	1.67	52.5	46.3	20,243	40,373
			1	1.85				
			2	2.03				
			3	2.21				
			4	2.50	50.8	34.4	23,474	46,835
Nylon a	2M2HT-montmorillonite	3.7	0	1.67	52.5	46.3	20,243	40,373
			1	1.89				
			2	2.14				
			3	2.34	51.9	36.3	22,676	45,238
			4	2.52	50.6	35.0	23,364	46,616
			5	2.73	50.5	33.0	23,952	47,791
Nylon a	ALA-montmorillonite	4.0	0	1.63	50.5	28.5	n.a.	n.a.
			1	1.82				
			2	2.05				

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			3	2.27				
Nylon a	2M2HT-montmorillonite	6.6	0	1.60	68.1	55.4	16.194	32,276
			1	1.78				
			2	1.91				
			3	2.10	67.8	46.0	17,575	35,036
			4	2.23				
			5	2.35	65.0	44.8	18,215	36,317
Nylon d	sepiolite	4.0	0	1.05				
			3	2.04				

The rate of increase is faster for acid-terminated ammonium cations at long residence times in a high-amine nylon matrix, as shown by the ALA-montmorillonite data in the graph below (Figure 6).

Example: 5: Injection molding of solid state polymerized nanocomposites

5 Solid-state polymerized nanocomposites based on nylons c and d mold easier with higher temperature setpoints than at lower temperature. Among these two nylons, the nylon d-based nanocomposites mold more easily than those based on the nylon c, perhaps because the nylon c matrix reaches a higher viscosity level than the nylon d. Lower pack and hold pressures can also be used.

10 In both cases, however, higher pack pressures and hold pressures than conventionally used to injection mold nylon 6,6 are preferred to better pack out the mold.

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## Molding Comparisons

Molding Conditions	Set Point Without SSP	Set Point After SSP	Actually Achieved After SSP
Pressures (psig)			
Injection Pressure:	2000	2000	2000
Injection Xfer Press.	2000	2000	2000
Pack Inj. Position	0.60	0.60	0.60
Pack Pressure	700-800	900	900
Hold Pressure	700-800	900	900
Back Pressure	100	100	100
Screw Speed (%)	30	30	30
Extrude Position	2.1	2.1	2.1
Cycle Times: (sec)			
Inject	1.0 - 2.0	1.0	1.0
Hold	15	15	15
Cure	15	15	15
Heaters: (°C)			
Rear	255	255	250
Middle	290	290	289
Front	295	295	290
Nozzle	295	295	290
Mold Temp. (°C)	93	93	93
Lube Type	None	None	None
Lube Level	None	None	None
Comments:		Molded	Molded
		Well	Well

Such higher pack and hold pressures usually also tend to increase tensile modulus and strength. Without SSP, lower molding temperatures are preferred for higher ductility in the molded parts due to less thermal degradation of the polymer. However, the higher ductility with SSP is instead achieved by higher molecular weight, thus allowing the use of the higher

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temperatures that are known to benefit the stiffness of the molded nanocomposite. In this way, an additional degree of processing freedom is introduced via the SSP process by which injection molding parameters can be adjusted to optimize the overall molding process and property spectrum.

Example 6: Mechanical properties for concentrate route using high amine nylon matrix

The use of a high amine end carrier nylon in a concentrate to enhance the properties induced by solid state polymerization of the final nanocomposite composition was evaluated. A high amine nylon concentrate comprising 17% ALA-montmorillonite in nylon d was then let down into three different resins having a range in molecular weight and amine/acid end group concentration, with and without subsequent solid-state polymerization prior to molding. A fairly intense screw design was used in the ZSK 40mm twin screw extruder with a feed rate of 100 lbs/hr (43.5 kg/hr) and screw speed of 250 rpm. The barrel zone temperatures were set at 270°C.

For the solid-state polymerization the polymerization dryer was set to 470°F (243°C) oil temperature from start to finish, giving a residence time of up to four hours at a 220°C resin temperature and 230°C shell temperature. Sample descriptions and mechanical properties are given in the table below.

Comment	Resin Type	% Ash	% Treated Clay	SSP hrs.	Tensile Strength (max), kpsi	Tensile Young's Modulus kpsi	Max. Elong., %	Flexural Modulus kpsi	Flexural Strength kpsi *	Notched IZOD ft lb/in	Un-notched IZOD ft lb/in	Mold Shrinkage mils/in
Control	Nylon d	0	0	0	11.38	455	47.7	450	16.0	0.79	39.6	19.4
	Nylon b	3.79	4.77	0	11.85	592	2.5	562	19.12	0.45	3.8	10.7
	Nylon c	3.99	5.02	0	13.29	570	15.7	554	18.98	0.60	5.4	10.5
	Nylon d	3.98	5.01	0	12.12	622	2.4	570	19.55	0.44	4.0	7.9
Mean		3.92		0	12.42	595	6.9	562	19.22	0.50	4.4	9.7
	Nylon b	3.79	4.77	4	13.63	603	22.6	560	18.6	0.87	19.1	9.8
	Nylon c	3.99	5.02	4	13.64	605	20.4	548	18.5	0.92	50.3	10.6
	Nylon d	3.98	5.01	4	14.27	661	18.1	577	19.3	0.79	42.2	7.4
Mean		3.92		4	13.84	623	20.4	562	18.79	0.86	37.2	9.3

\* Stress measured at 5% strain.

The previous table shows the beneficial effect of solid state polymerization in improving the ultimate mechanical properties of tensile strength and elongation, as well as both notched and un-notched Izod impact strength. Its strong effect on nanocomposites comprising the ALA-

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montmorillonite compensates any molecular weight degradation of the nylon that might have occurred during compounding.

The effects of the parameters can be analyzed more quantitatively by use of the neural network CAD/Chem software (AIWare, Cleveland, OH). In this approach, the nylons are described by their nominal weight-average molecular weight and the nominal ratio of amine/acid end groups. The mineral content of the nanocomposite is retained as a correlating variable to account for the minor differences between samples. On this basis, the following linear correlation coefficients are obtained. SSP refers to the solid state polymerization time, in hours.

	Mw	Amine/Acid End Groups	% Ash	SSP
Max TS	0.11	0.17	0.39	0.68
E tensile	-0.14	-0.02	0.45	0.35
Ult Elong.	0.14	0.26	-0.39	0.41
E flex	-0.19	0.05	0.25	0.09
E 5% flex	-0.16	0.12	0.29	-0.03
Notched Izod	0.45	0.02	-0.22	0.65
Un-not Izod	0.00	0.37	-0.15	0.77
Shrinkage	0.22	0.07	-0.08	-0.02

These results show that solid state polymerization generally increases tensile properties along with both types of Izod impact strength, while having a negligible overall effect on flex properties. A higher initial molecular weight in the nylon (prior to compounding) could also be somewhat beneficial for notched Izod impact strength, but does not positively affect properties. A higher amine/acid end group ratio is seen to be generally advantageous for ductility (elongation) and toughness (un-notched Izod impact strength) as it helps to maintain nylon molecular weight by counteracting the additional acidity introduced by the clay treatment.

However, strong parameter interactions not apparent in the above table do occur and can be seen in the following response surfaces. With 4 hours solid state polymerization time, a nanocomposite comprising 4.9% by weight ALA-montmorillonite (3.9% mineral ash) in a 40,000 Mw nylon having balanced end groups is predicted to have the following properties: 14.00 Kpsi tensile strength, 612 Kpsi Young's modulus, 21.6% ultimate elongation, 558 Kpsi

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flex modulus, 18.68 Kpsi flex stress at 5% strain (below breaking strain), 0.91 ft-lb/in notched Izod, 43.9 ft-lb/in un-notched Izod and 9.5 mil/in shrinkage.

Figure 7 shows increasing tensile strength with SSP time when nanoclay is present, but not in the neat nylon.

The ductility and toughness of nanocomposites, however, are increased significantly by solid state polymerization and to a lesser extent by higher amine/acid ratio and initial molecular weight of the nylon (Figures 8, 9 and 10). The ALA-montmorillonite concentration in the last two figures is 4.9%.

Stiffness (tensile modulus) is slightly increased by solid state polymerization, perhaps through network formation between the high MW nylon and the clay by reactive tethering of the nylon polymer molecules to the ammonium ions adsorbed on the clay surface (Figure 11).

#### Example 7: Data Tabulation

A comprehensive listing of composition, SSP time and mechanical property data is given in the table below for all of the ALA-montmorillonite, 2M2HT-montmorillonite, 2MBHT-montmorillonite and sepiolite nanocomposite preparations involving solid state polymerization.

Nylon Type	Clay Type	Mineral Ash (%wt)	Total Clay (%wt)	Silane (wt% on Clay)	S.S.P. Time (Hrs.)	Max Tens Strength (kpsi)	Tens Brk Elongat. (%)	Tensile Modulus (kpsi)	Flexural Modulus (kpsi)	Flexural Strength (kpsi)	IZOD Not. (ft lb/in)	IZOD Unnot. (ft lb/in)	Breaks / Non-Breaks	Mold Shrinkage (mils/in)
a	2M2HT-mont.	4.1	6.6	0.0	0	12.12	4.4	590	531	17.8	0.52	16.2	(5/0)	
a	2M2HT-mont.	4.1	6.6	0.0	5	11.71	19.5	548	549	17.7	0.80	63.0		
a	2M2HT-mont.	2.3	3.7	0.0	0	11.87	17.1	522	494	17.3	0.69	31.6	(4/1)	
a	2M2HT-mont.	2.3	3.7	0.0	4	11.96	96.6	481	507	17.1	0.95	50.6		
a	2M2HT-mont.	2.3	3.7	0.0	5	11.60	73.3	513	541	17.7	0.84	63.1		
a	ALA-mont.	3.2	4.0	0.0	0	12.81	4.6	548	507	17.9	0.37	3.4	(5/0)	
a	ALA-mont.	3.2	4.0	0.0	3	12.02	24.3	528	515	17.3	0.76	45.1		
c	2MBHT-mont.	5.1	8.4	2.0	0	13.97	5.9	687	701	20.6	0.52	11.5	(5/0)	
c	2MBHT-mont.	5.1	8.4	2.0	2	13.53	11.7	653	695	21.1	0.59	10.9		
c	2MBHT-mont.	7.5	12.2	2.0	0	12.86	2.0	754	626	20.4	0.69	14.5	(5/0)	
c	2MBHT-mont.	7.5	12.2	2.0	4	13.24	2.2	734	615	19.7	0.71	38.3		
b	2M2HT-mont.	3.9	6.2	0.0	0	11.16	5.4	544	524	16.4	0.50	12.9	(5/0)	
b	2M2HT-mont.	3.9	6.2	0.0	3	11.91	7.4	537	540	17.6	0.57	22.9		
b	ALA-mont.	0.0	0.0		0	11.38	47.7	455	450	16.0	0.79	39.6	(1/3)	19.4
b	ALA-mont.	3.8	4.8	2.0	0	11.85	2.5	592	562	19.1	0.45	3.8	(5/0)	10.7
b	ALA-mont.	3.8	4.8	2.0	4	13.63	22.6	587	560	18.6	0.87	19.1	(3/0)	9.8
c	ALA-mont.	4.0	5.0	2.0	0	13.29	15.7	570	554	19.0	0.60	5.4	(5/0)	10.5
c	ALA-mont.	4.0	5.0	2.0	4	13.64	20.4	587	548	18.5	0.92	50.3	(0/4)	10.6
d	ALA-mont.	4.0	5.0	2.0	0	12.12	2.4	622	570	19.6	0.44	4.0	(5/0)	7.9
d	ALA-mont.	4.0	5.0	2.0	4	14.27	18.1	647	577	19.3	0.79	42.2	(2/3)	7.4
d	Sepiolite	3.5	4.1	0.0	0	12.94	3.3	543	504	17.9	0.58	5.5	(5/0)	n.a.
d	Sepiolite	3.5	4.1	0.0	4	12.68	10.6	473	466	16.9	0.95	42.3	(1/4)	13.7
c	Sepiolite	2.5	2.9	2.0	0	11.81	28.3	467	446	15.8	0.91	42.6	(1/4)	16.8
c	Sepiolite	2.5	2.9	2.0	4	11.56	36.2	413	401	14.8	1.22	45.3	(0/5)	16.5

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Aminoacid organoclay is seen to provide the most favorable combination of nanocomposite properties following SSP. However, it may cause more embrittlement than other clay types if SSP is not practiced. The acid functionalization is believed to compete for the amine end groups on the nylon chains, thus upsetting the end group balance and degrading nylon molecular weight during compounding. Higher initial molecular weight or amine/acid end group ratio in the selected nylon would help to counteract this effect, but SSP preferably would be performed following compounding to restore or even further increase the nylon molecular weight. Pristine sepiolite is observed to be less destructive to ductility and toughness than is the montmorillonite.

Nanocomposite material compounded with a single pass through the Farrell Continuous Mixer, which tends to impart high modulus but embrittlement in nanocomposites, could be solid-state polymerized to restore ductility and toughness along with possible increase in tensile strength. The combination of FCM compounding with SSP would represent a low cost process to a ductile and tough, yet stiff, nanocomposite.

All of the compositions, processes, and apparatus disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and processes of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions, processes, and apparatus and in the steps or in the sequence of steps of the processes described herein without departing from the concept, spirit and scope of the invention. More specifically, it will be apparent that certain agents which are chemically related may be substituted for the agents described herein while the same or similar results would be achieved. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the invention.



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**CLAIMS:**

1. A process to prepare a polymer nanocomposite composition, the process comprising:  
forming a flowable mixture of a polyamide and a silicate material;  
dissociating at least about 50% but not all of the silicate material to form a dissociated  
5 mixture; and  
subjecting the dissociated mixture to solid state polymerization conditions to polymerize  
the polyamide and to form the polymer nanocomposite composition.
2. The process of claim 1, wherein the polyamide is nylon 6, nylon 6,6, nylon 4,6, nylon  
6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons, or  
10 copolymers thereof.
3. The process of claim 1, wherein the silicate is montmorillonite, nontronite, beidellite,  
volkonskoite, hectorite, synthetic or natural sepiolite, saponite, sauconite, magadite, or  
kenyaite.
4. The process of claim 1, wherein the composition further comprises at least one  
15 surfactant, nucleating agent, coupling agent, filler, plasticizer, impact modifier, chain  
extender, compatibilizer, colorant, mold release lubricant, antistatic agent, pigment, or  
fire retardant.
5. The process of claim 4, wherein the coupling agent is a silane, titanate, or a zirconate.
6. The process of claim 5, wherein the coupling agent is gamma-  
20 aminopropyltriethoxysilane.
7. The process of claim 6, wherein the concentration of gamma- aminopropyltriethoxysilane  
in the polymer nanocomposite composition is between about 0.5 weight percent and  
about 5 weight percent of the silicate material.
8. The process of claim 1, wherein the concentration of silicate material in the polymer  
25 nanocomposite composition is between about 0.1 weight percent and about 12.0 weight  
percent of the polymer nanocomposite composition.

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9. The process of claim 1, wherein the concentration of silicate material in the polymer nanocomposite composition is between about 0.5 weight percent and about 6.0 weight percent of the polymer nanocomposite composition.
10. The process of claim 1, wherein the silicate material is dissociated by a mechanical unit,  
5 thermal shock, pressure alteration, or ultrasonics.
11. The process of claim 10, wherein the mechanical unit is a stirrer, Banbury<sup>®</sup> type mixers, Brabender<sup>®</sup> type mixers, Farrel<sup>®</sup> continuous mixers, or extruders.
12. The process of claim 11, wherein the extruders are single screw extruders or twin screw extruders.
- 10 13. The process of claim 12, wherein the twin screw extruder is a co-rotating fully intermeshing twin screw extruder.
14. The process of claim 1, wherein the silicate material is dissociated by two or more dissociating methods selected from the group consisting of a mechanical unit, thermal shock, pressure alteration, and ultrasonics.
- 15 15. The process of claim 1, wherein the silicate material is added as a mixture of silicate material and a carrier polymer.
16. The process of claim 15, wherein said carrier polymer comprises polyamide, ethylene-propylene rubber, ethylene-propylene diene rubber, ethylene-ethylacrylate, ethylene-ethylmethacrylate or ethylene methacrylate.
- 20 17. The process of claim 16, wherein the polyamide carrier polymer is nylon 6, nylon 6,6, nylon 4,6, nylon 6,9, nylon 6,10, nylon 6,12, nylon 11, nylon 12, amorphous nylons, aromatic nylons, or copolymers thereof.
18. The process of claim 15, wherein the carrier polymer is of a different weight average molecular weight than the polyamide in the flowable mixture.

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19. The process of claim 15, wherein said carrier polymer is a polymer other than a polyamide.
20. The process of claim 15, wherein the carrier polymer has a weight average molecular weight of about 10,000 to about 40,000 D.
- 5 21. The process of claim 1, wherein said flowable mixture further comprises a monomer.
22. The process of claim 21, wherein the monomer comprises  $\epsilon$ -caprolactam, lauryllactam,  $\epsilon$ -caprolactone, or lauryllactone.
23. The process of claim 21, wherein said process further comprises polymerizing said monomer.
- 10 24. The process of claim 1, further comprising adding additional polyamide to the flowable mixture during the dissociating step.
25. The process of claim 1, wherein the silicate material is treated with an ammonium ion of the formula:  
$$^+NR_aR_bR_cR_d$$
  
15 wherein  $R_a$ ,  $R_b$  and  $R_c$  are hydrogen (H) and  
and  $R_d$  includes a carboxylic acid moiety.
26. The process of claim 1, wherein the silicate is treated with an azine cationic dye.
27. The process of claim 26, wherein the azine cationic dye is a nigrosine or an anthracine.
28. The process of claim 4, wherein the filler is carbon fiber, glass fiber, kaolin clay,  
20 wollastonite, mica or talc.
29. The process of claim 4, wherein the compatibilizer is an acid-modified hydrocarbon polymer.

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30. The process of claim 4, wherein the compatibilizer is maleic anhydride-grafted polyethylene, maleic anhydride-grafted polypropylene, or maleic anhydride-grafted ethylene-butylene-styrene block copolymer.
31. The process of claim 4, wherein the lubricant is an alkyl amine, stearamide, di-aluminum  
5 stearate, or tri-aluminum stearate.
32. The process of claim 4, wherein the impact modifier is ethylene-propylene rubber, ethylene-propylene diene rubber, methacrylate-butadiene-styrene (with core-shell morphology), poly(butylacrylate) with or without carboxyl modification, poly(ethylene  
10 acrylate), poly(ethylene methacrylate), poly(ethylene acrylic acid), poly(ethylene acrylate) ionomers, poly(ethylene methacrylate acrylic acid) terpolymer, poly(styrene-butadiene) block copolymers, poly(styrene-butadiene-styrene) block terpolymers, poly(styrene-ethylene/butylene-styrene) block terpolymers, or poly(styrene-ethylene/butylene-styrene carboxylate) block terpolymers.
33. The process of claim 1, wherein the nanocomposite composition comprises polyamide  
15 crystalline regions less than about 1.0  $\mu\text{m}$ .
34. The process of claim 1, wherein the nanocomposite composition is in the form of a fiber, film or a molded article.
35. The process of claim 1, wherein the solid state polymerization comprises heating the  
20 dissociated mixture to a temperature in the range of about 200°C to about 240°C for a period of about 2 to about 5 hours.
36. The process of claim 1, wherein the solid state polymerization comprises:  
adding a catalyst; and  
heating the dissociated mixture to a temperature at least 20°C below the melting or  
softening point of the polyamide for a period of about 0.5 to about 5 hours;  
25 wherein:

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the molecular weight of the nanocomposite composition formed in the presence of the catalyst is greater than the molecular weight of the nanocomposite composition formed in the absence of the catalyst.

37. The process of claim 1, further comprising heat treating the nanocomposite composition to a temperature in the range of about 200°C to about 240°C for a period of about 2 to about 5 hours.
38. A nanocomposite composition comprising a polyamide and a silicate, wherein the polyamide has a concentration of amine end groups at least 10 mole % greater than the concentration of the carboxylic acid end groups.
39. A nanocomposite composition comprising a polyamide and a silicate, wherein the polyamide has a weight average molecular weight in the range of about 30,000 D to about 40,000 D.
40. A nanocomposite composition comprising a polyamide and a silicate, wherein the polyamide has a weight average molecular weight in the range of at least 40,000 D.
41. A nanocomposite composition comprising a polyamide and a silicate, wherein the silicate is treated with an ammonium ion of the formula:
- $$^+NR_aR_bR_cR_d$$
- wherein  $R_a$ ,  $R_b$  and  $R_c$  is hydrogen (H) and  $R_d$  includes a carboxylic acid moiety.

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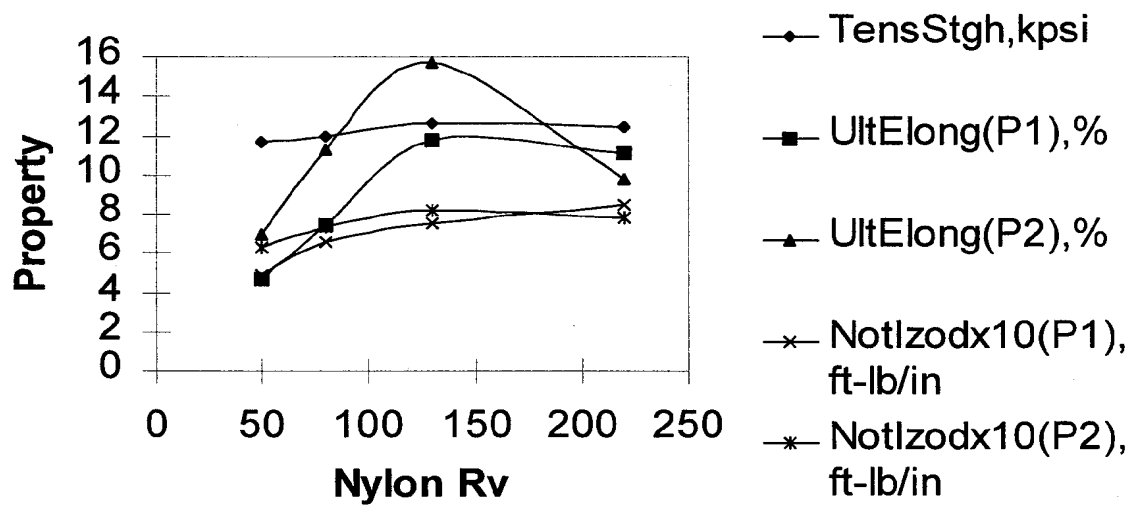


FIG. 1

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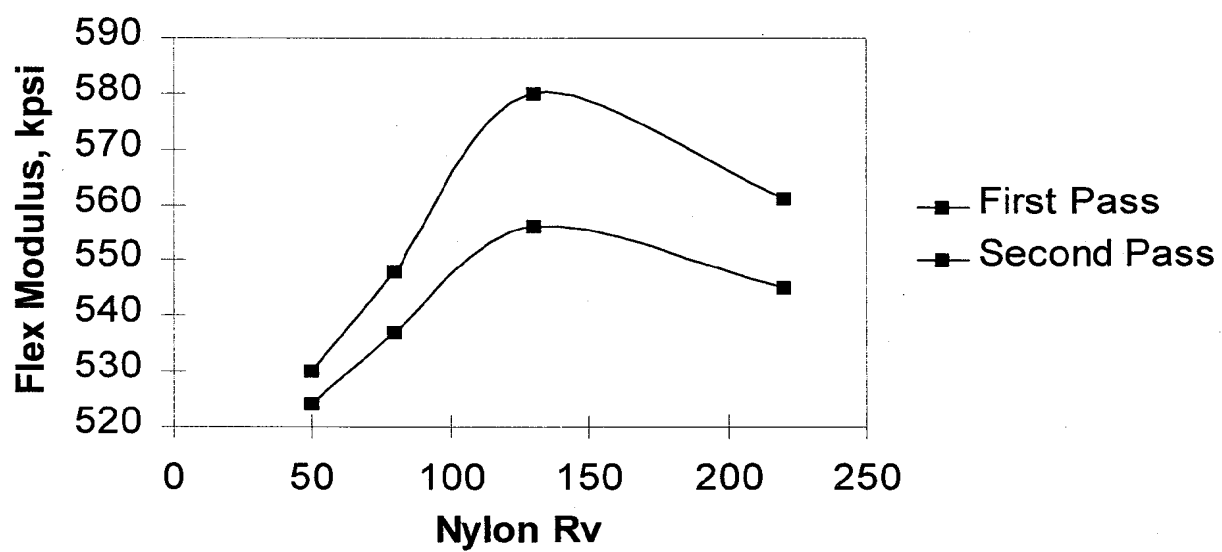


FIG. 2

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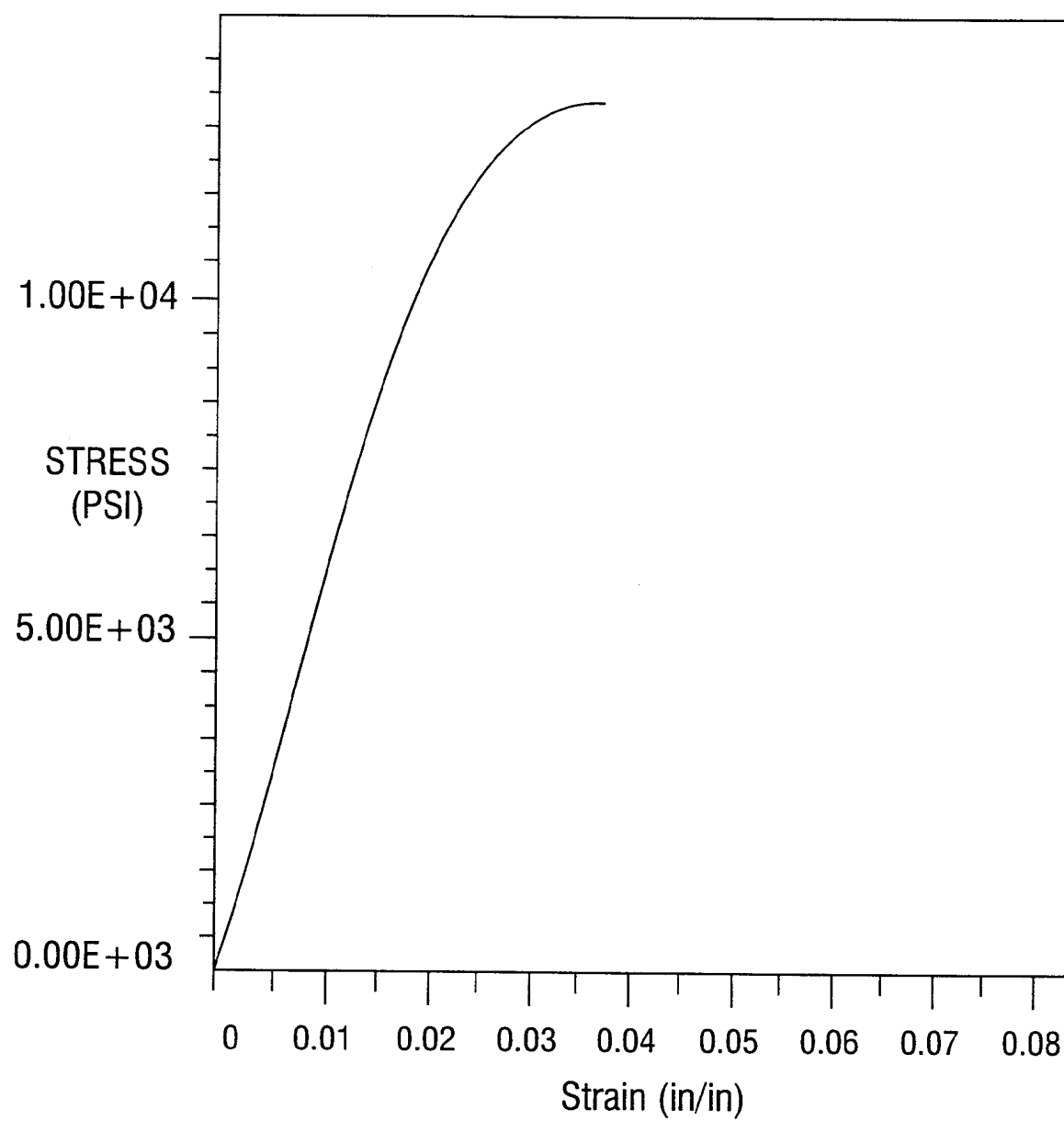


FIG. 3



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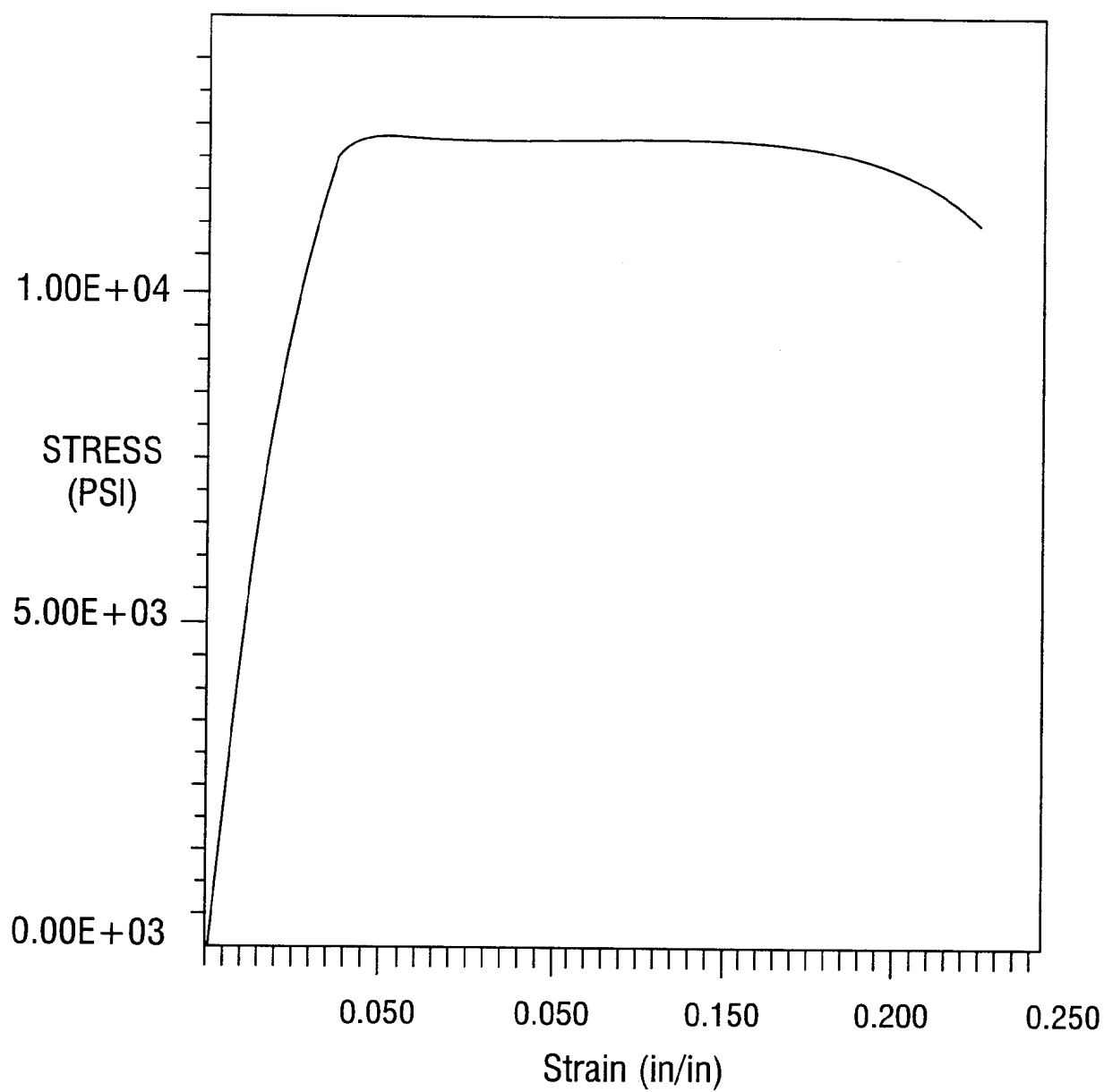


FIG. 4

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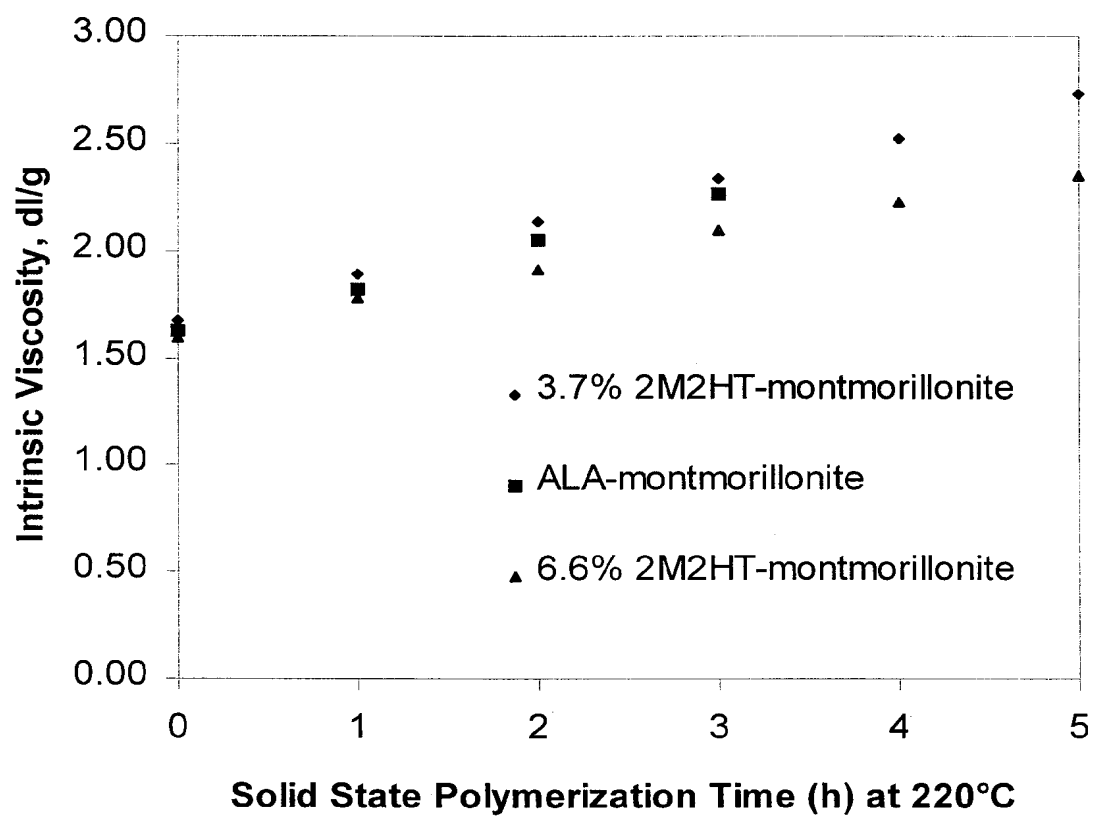


FIG. 5

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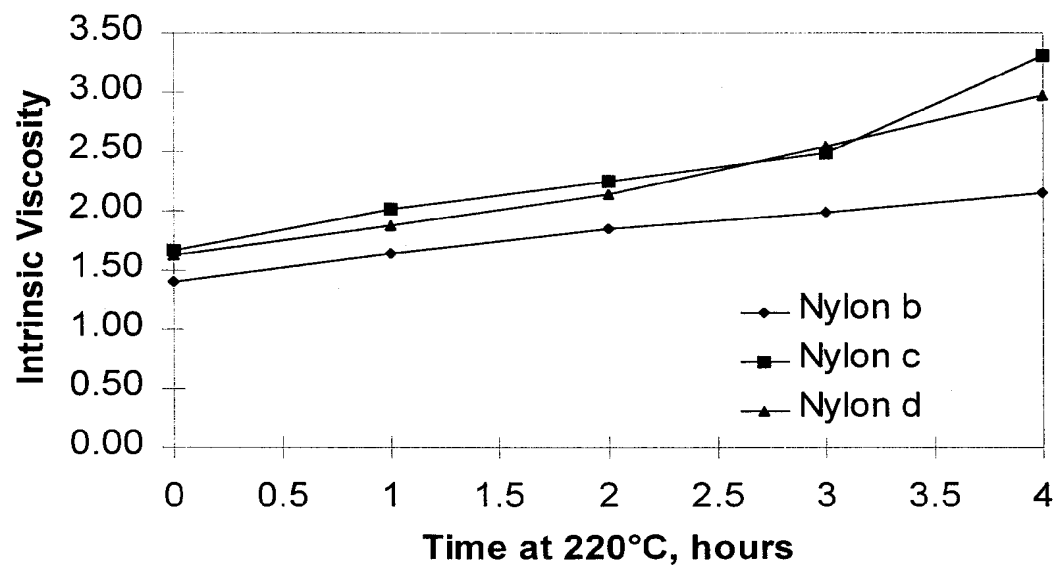


FIG. 6

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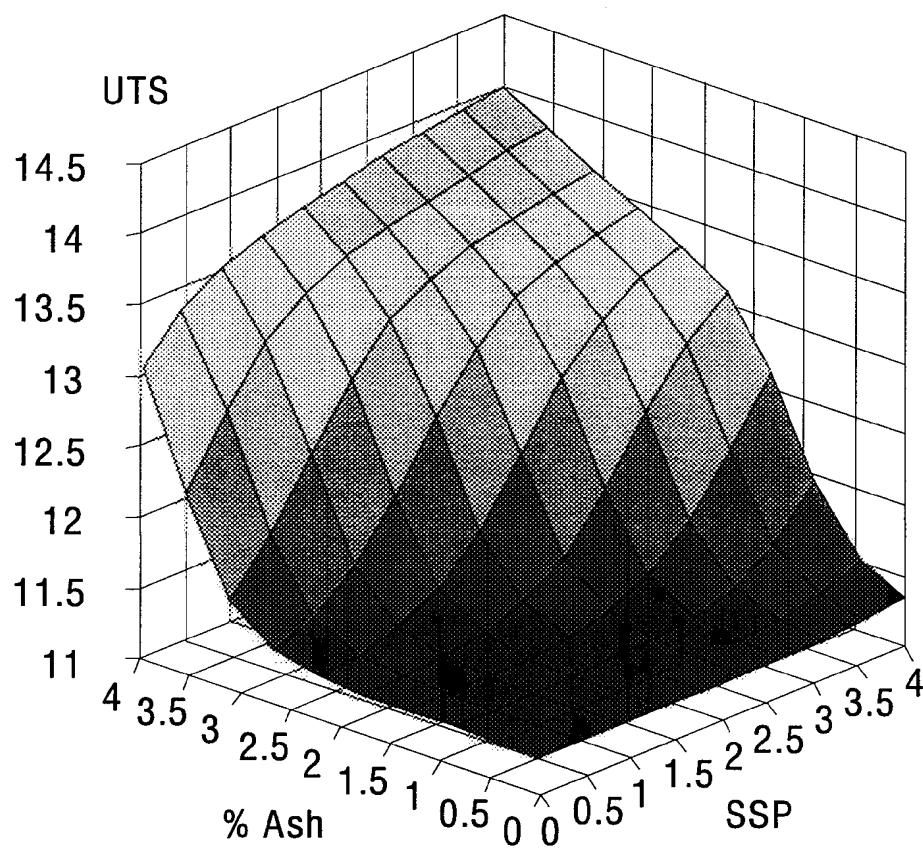


FIG. 7

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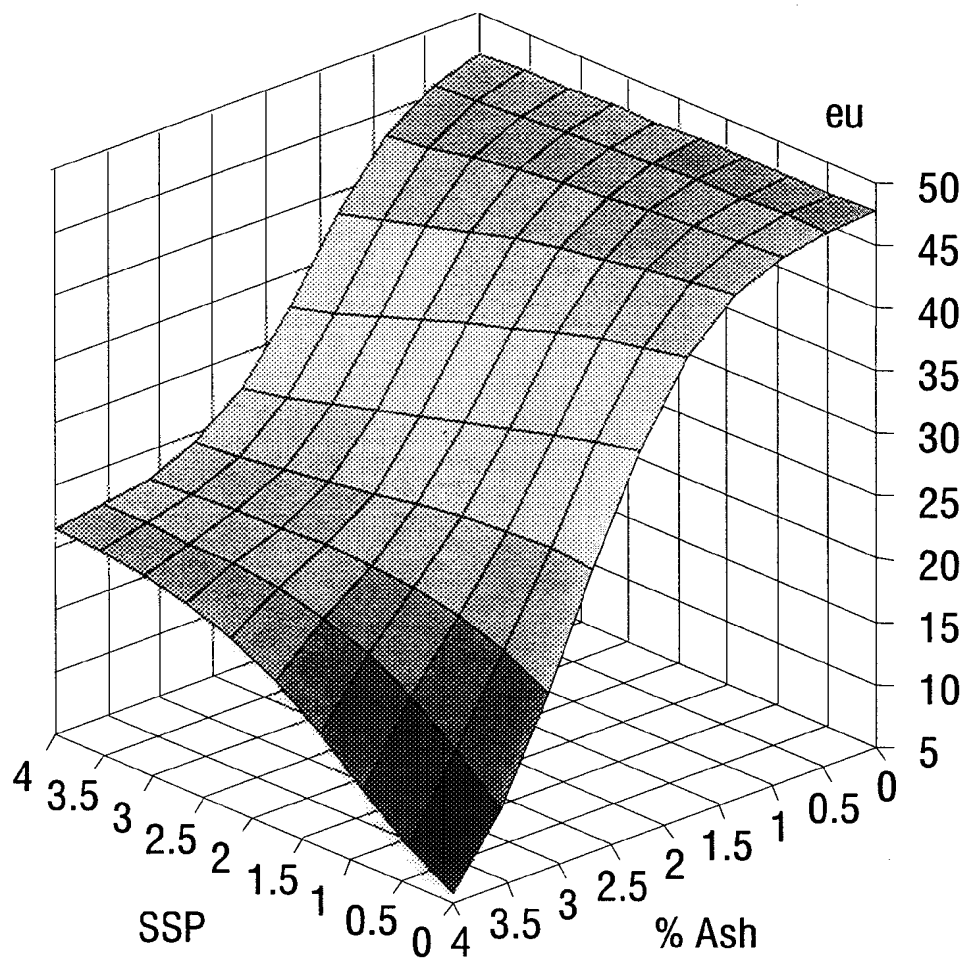


FIG. 8

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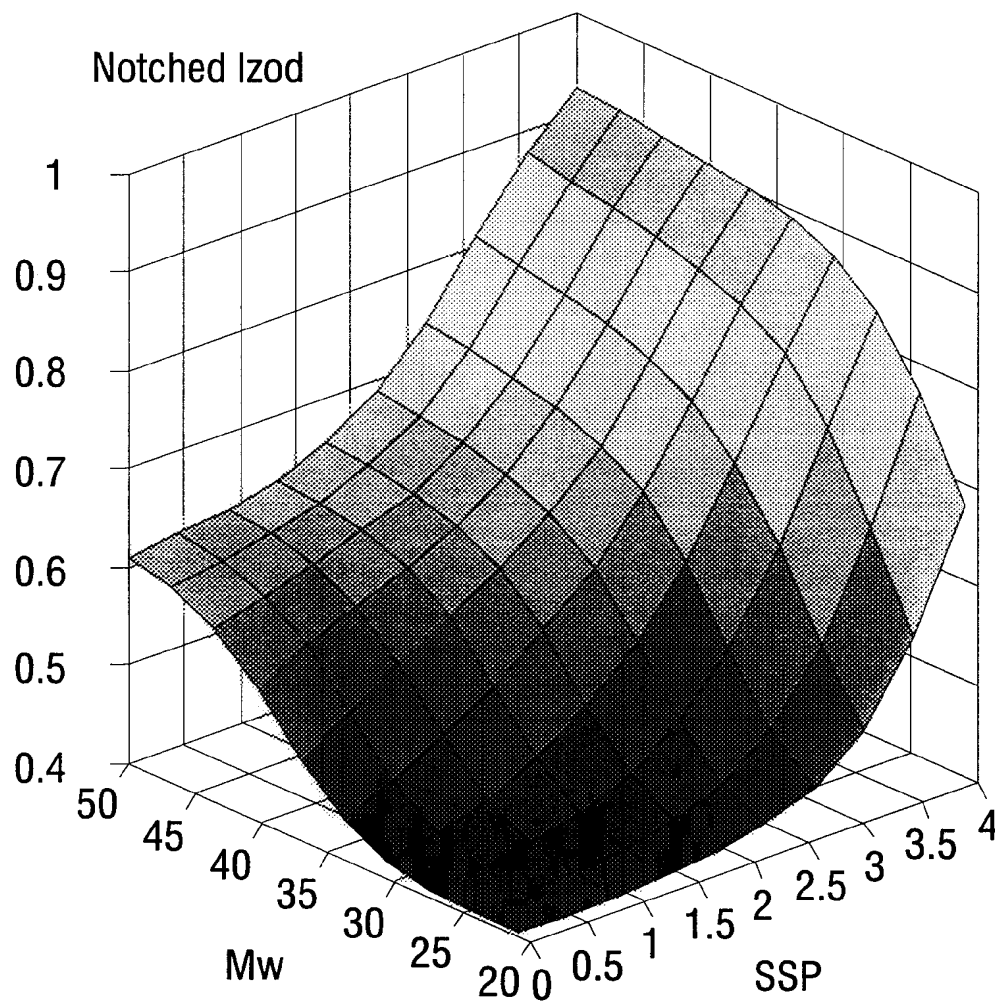


FIG. 9

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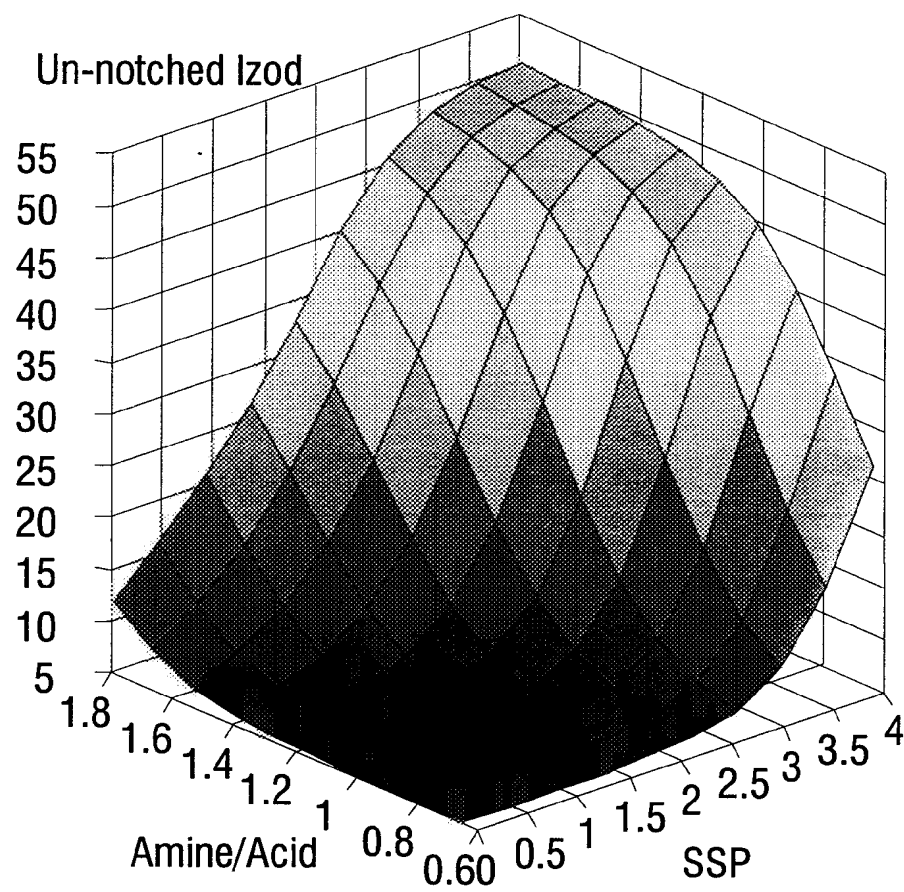


FIG. 10

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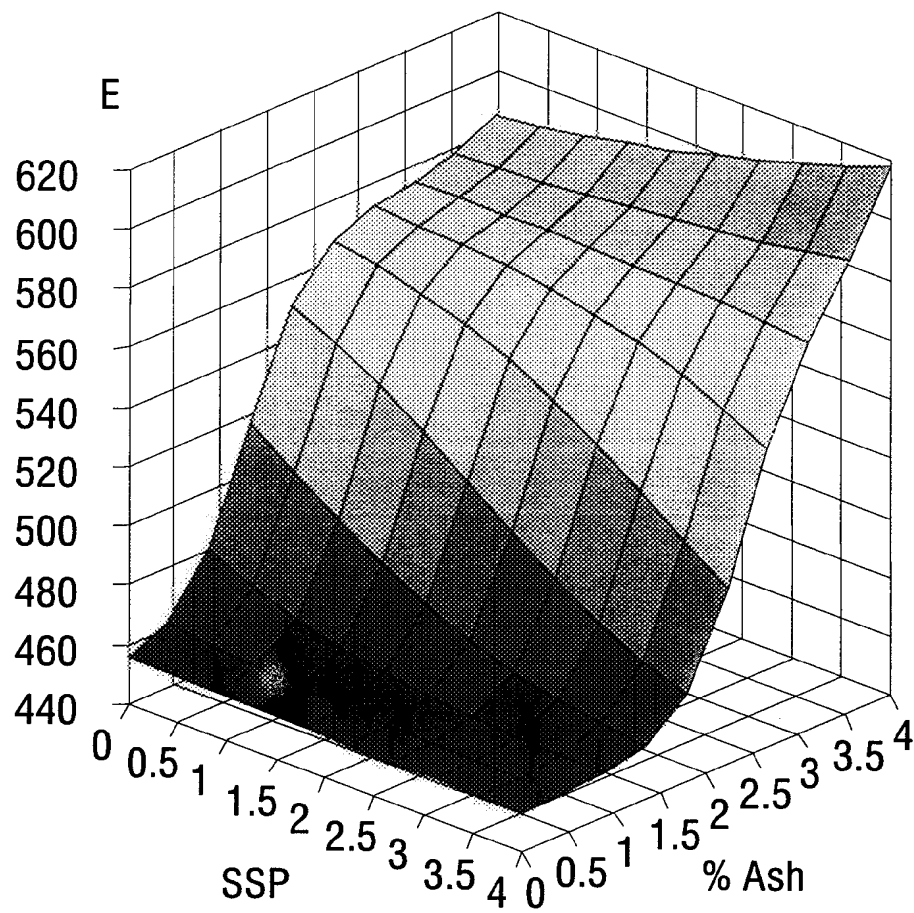


FIG. 11



## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US99/03097

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(6) :B29D 22/00

US CL :524/445

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 524/445

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,739,007 A (OKADA et al) 19 April 1988, col. 12, lines 32-43.	38-41
Y	US 4,810,734 A (KAWASUMI et al) 07 March 1989, col. 10, lines 64-68 and col. 11, lines 1-8 and col. 12, line 12.	38-41
Y	US 5,102,948 A (DEGUCHI et al) 07 April 1992, col. 13, lines 55-65.	38-41



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G* document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means	
*P* document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

26 APRIL 1999

Date of mailing of the international search report

11 MAY 1999

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